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10 (54) [Title of the Invention]

POLYPROPYLENE-BASED RESIN FOAMED MOLDED PRODUCT AND
METHOD OF MANUFACTURING THE SAME

(57) [Abstract]

[Problem] Obtain foamed particles and a foamed molded
15 product having a low density, a high uniformity, and a
controllable heat resistance to steam, and foaming
modified resin particles and foamable resin particles
for obtaining them.

[Solving Means] Provided are foaming modified
20 polypropylene-based resin particles obtained by
heat-treating polypropylene-based resin particles
mainly containing a propylene copolymer of ethylene and
(or) another α -olefin, characterized in that the
principal endothermic peak temperature of a DSC curve
25 obtained by scanning differential calorimetry is higher
by 5°C or more than that of the polypropylene-based
resin particles before the heat treatment, foamable

polypropylene-based resin particles,
polypropylene-based resin foamed particles, and a
polypropylene-based resin foamed molded product
obtained from the foaming modified polypropylene-based
5 resin particles, and methods of manufacturing these
particles and product..

[What Is Claimed Is:]

[Claim 1]

Foaming modified polypropylene-based resin particles obtained by heat-treating polypropylene-based resin particles mainly containing a propylene copolymer of ethylene and (or) another α -olefin, characterized in that a principal endothermic peak temperature of a DSC curve obtained by scanning differential calorimetry is higher by not less than 5°C than a principal endothermic peak temperature of the polypropylene-based resin particles before the heat treatment.

[Claim 2]

The foaming modified polypropylene-based resin particles according to claim 1, wherein another endothermic peak exists at a temperature lower by not less than 7°C than the principal endothermic peak temperature before the heat treatment.

[Claim 3]

The foaming modified polypropylene-based resin particles according to claim 1 or 2, wherein the propylene copolymer is a random copolymer.

[Claim 4]

Foamable polypropylene-based resin particles characterized by being obtained by impregnating foaming modified polypropylene-based resin particles cited in any one of claims 1 to 3 with a foaming agent.

[Claim 5]

Polypropylene-based resin foamed particles
characterized by being obtained by prefoaming foamable
polypropylene-based resin particles cited in claim 4.

[Claim 6]

5 Polypropylene-based resin foamed particles
characterized by being obtained by pressurizing and
prefoaming polypropylene-based resin foamed particles
cited in claim 5 once or a plurality of number of times
in a gas ambient containing a foaming agent.

10 [Claim 7]

A polypropylene-based resin foamed molded product
characterized by being obtained by molding
polypropylene-based resin foamed particles cited in
claim 5 or 6 in a mold.

15 [Claim 8]

A method of manufacturing foaming modified
polypropylene-based resin particles, characterized by
comprising heat-treating polypropylene-based resin
particles mainly containing a propylene copolymer of
20 ethylene and (or) another α -olefin within a temperature
range from a principal endothermic peak temperature of
a DSC curve, which is obtained by scanning differential
calorimetry, of the polypropylene-based resin particles
to a temperature higher by 15°C than the principal
25 endothermic peak temperature.

[Claim 9]

A method of manufacturing foamable

polypropylene-based resin particles, characterized by
comprising impregnating foaming modified
polypropylene-based resin particles obtained by a
method cited in claim 8 with a foaming agent at a
5 temperature lower than a Vicat softening temperature of
polypropylene-based resin particles before a heat
treatment.

[Claim 10]

A method of manufacturing polypropylene-based
10 resin foamed particles, characterized by comprising
prefoaming foamable polypropylene-based resin particles
obtained by a method cited in claim 9.

[Claim 11]

A method of manufacturing polypropylene-based
15 resin foamed particles, characterized by comprising
pressurizing and prefoaming polypropylene-based resin
foamed particles obtained by a method cited in claim 10
once or a plurality of number of times in a gas ambient
containing a foaming agent.

20 [Claim 12]

A method of manufacturing a polypropylene-based
resin foamed molded product, characterized by
comprising molding polypropylene-based resin foamed
particles obtained by a method cited in claim 10 or 11
25 in a mold.

[Detailed Description of the Invention]

[0001]

[Technical Field to Which the Invention Belongs]

The present invention relates to foaming modified polypropylene-based resin particles, foamable polypropylene-based resin particles,

- 5 polypropylene-based resin foamed particles, a polypropylene-based resin foamed molded product, and methods of manufacturing these particles and product. More specifically, the present invention relates to foaming modified polypropylene-based resin particles
10 and foamable polypropylene-based resin particles capable of obtaining low-density uniform foamed particles, polypropylene-based resin foamed particles, a polypropylene-based resin foamed molded product, and methods of manufacturing these particles and product.
15 The foamable polypropylene-based resin particles of the present invention do not largely change the foaming density even when a storage time elapses before they are foamed, and the foamed molded product deriving from the resin particles is substantially not crosslinked,
20 has excellent recycling properties and a low bulk density, and can improve the heat resistance to steam.

[0002]

[Prior Art and Problems That the Invention Is to Solve]

- A polystyrene-based resin, polyethylene-based
25 resin, or polypropylene-based resin is generally used as a base resin of a foamed molded product which is molded in a mold. However, when a polystyrene-based

resin is used as the base resin, the obtained foamed molded product is brittle and inferior in chemical resistance. To solve this problem, a foamed molded product using a polyethylene-based resin as the base is
5 proposed. When this resin is used as the base, a soft tough foamed molded product is obtained, but a crosslinking process is necessary to decrease the density. As a consequence, the recycling properties deteriorate.

10 [0003]

When a polypropylene-based resin is used as the base, the density can be decreased although substantially no crosslinking is performed (Japanese Patent Publication No. 56-1344). On the other hand, a
15 high softening temperature of the polypropylene-based resin raises the processing temperatures of foaming and molding. This increases the installation cost of, e.g., a foaming machine and molding machine, and significantly deteriorates the durability of the metal
20 mold. Also, the polypropylene-based resin can more or less increase the heat resistance to steam of the obtained foam when the contents of, e.g., polyethylene and a plasticizer are controlled, but the heat resistance cannot be greatly increased. In addition,
25 to soften the polypropylene-based resin, methods such as crosslinking of polypropylene and a readily crosslinkable polymer such as polyethylene or

polybutadiene (Japanese Patent Publication
No. 60-28856) and crosslinking of polypropylene
(Japanese Patent Publication Nos. 60-168632 and
3-48936) are proposed. Especially when the ethylene
5 component increases, however, a crosslinking process is
necessary to decrease the density of foam, and this
deteriorates the recycling properties.

[0004]

Any of the resins described above has low gas
10 barrier properties, so a foaming agent disappears
within a short time even if it is contained. Therefore,
a foam obtained from any of these resins has a high
density and is often nonuniform. Also, when foamable
resin particles obtained from any of these resins are
15 opened to the atmosphere and foamed after an elapse of
a certain time, the density of the foamed particles
abruptly increases as the elapsed time prolongs. As a
method of manufacturing foamable polyolefin resin
particles, Japanese Patent Publication No. 2-59171 has
20 proposed a method of manufacturing spherical foamable
polyolefin resin particles. In this method, however,
when resin particles for foaming are to be impregnated
with a foaming agent, both the resin particles and
foaming agent are heated to a temperature from the
25 melting point of the resin particles - 5°C to the
melting point + 10°C. Since this requires an
impregnating installation which can resist high

temperatures and high pressures, the installation cost rises. Also, when the foamable resin particles are opened to the atmosphere and foamed after an elapse of a certain time, a high-density foam is often obtained.

5 This decreases the effect of heat-treating the resin particles.

[0005]

Furthermore, Japanese Patent Publication No. 3-2890 describes a method of manufacturing

10 spherical polyolefin resin particles. However, this reference discloses neither foamable resin particles capable of suppressing the increase in density even when opened to the atmosphere and foamed after an elapse of a certain time, nor a method of controlling

15 the crystallinity of the resin particles. As a method of manufacturing low-density foamed particles, a method such as a DOKAN method (Japanese Patent Publication No. 59-23731) by which resin particles impregnated with a foaming agent are released in a low-pressure ambient

20 is generally known. Although this method can manufacture low-density foamed particles, it is difficult to obtain foamed particles having a uniform density. Also, in this method, the resin particles are impregnated with the foaming agent at a temperature

25 equal to or higher than the Vicat softening temperature of the resin particles. Since this requires an impregnating installation capable of resisting high

pressures, the installation cost rises. In addition, the resin particles easily bond to each other, so the solid/liquid ratio cannot be raised. Accordingly, the amount of foamed particles obtained by one batch of manufacture is unsatisfactory. Furthermore, the principal endothermic peak temperature of a DSC curve, which is obtained by scanning differential calorimetry, of the foamed particles obtained by this method is the same as that of the resin particles. This makes it impossible to control the heat resistance to steam.

[0006]

[Means of Solving the Problems]

The present inventors made extensive studies on the present situation as described above, and have found that it is possible to obtain foaming modified polypropylene-based resin particles by heat-treating polypropylene-based resin particles within a temperature range from the principal endothermic peak temperature of the polypropylene-based resin particles to a temperature higher by 15°C than that, and to obtain foamable polypropylene-based resin particles which do not largely change the density of foamed particles even when a storage time elapses before foaming, by impregnating the foaming modified polypropylene-based resin particles with a foaming agent at a temperature lower than the Vicat softening temperature of the polypropylene-based resin particles.

The present inventors have also found that it is possible, by prefoaming the foamable polypropylene-based resin particles as described above, to obtain polypropylene-based resin foamed particles and a polypropylene-based resin foamed molded product which are substantially not crosslinked and superior in recycling properties, and have a low bulk density and a controllable heat resistance to steam. Note that in this invention, the principal endothermic peak temperature of the polypropylene-based resin particles before the heat treatment is a temperature at which an endothermic peak is found on a DSC curve obtained by scanning differential calorimetry. More specifically, if there is only one endothermic peak, the principal endothermic peak temperature is the temperature of the peak, and, if there are a plurality of endothermic peaks, the principal endothermic peak temperature is the temperature of the highest peak.

[0007]

Accordingly, the present invention provides foaming modified polypropylene-based resin particles obtained by heat-treating polypropylene-based resin particles mainly containing a propylene copolymer of ethylene and (or) another α -olefin, characterized in that the principal endothermic peak temperature of a DSC curve obtained by scanning differential calorimetry is higher by 5°C or more than that of the

polypropylene-based resin particles before the heat treatment.

[0008]

There are also provided foamable

- 5 polypropylene-based resin particles characterized by being obtained by impregnating the foaming modified polypropylene-based resin particles described above with a foaming agent. There are also provided polypropylene-based resin foamed particles
- 10 characterized by being obtained by prefoaming the foamable polypropylene-based resin particles described above. There are also provided polypropylene-based resin foamed particles characterized by being obtained by pressurizing and prefoaming the polypropylene-based
- 15 resin foamed particles described above once or a plurality of number of times in a gas ambient containing a foaming agent. In addition, there is provided a polypropylene-based resin foamed molded product characterized by being obtained by molding the
- 20 polypropylene-based resin foamed particles described above in a mold. Furthermore, there is provided a method of manufacturing foaming modified polypropylene-based resin particles, characterized by comprising heat-treating polypropylene-based resin
- 25 particles mainly containing a propylene copolymer of ethylene and (or) another α -olefin within a temperature range from the principal endothermic peak temperature

of a DSC curve, which is obtained by scanning differential calorimetry, of the polypropylene-based resin particles to a temperature higher by 15°C than that. There is also provided a method of manufacturing
5 foamable polypropylene-based resin particles, characterized by comprising impregnating foaming modified polypropylene-based resin particles obtained by the above method with a foaming agent at a temperature lower than the Vicat softening temperature
10 of the polypropylene-based resin particles before the heat treatment. There is also provided a method of manufacturing polypropylene-based resin foamed particles, characterized by comprising prefoaming foamable polypropylene-based resin particles obtained
15 by the above method. In addition, there is provided a method of manufacturing polypropylene-based resin foamed particles, characterized by comprising pressurizing and prefoaming polypropylene-based resin foamed particles obtained by the above method once or a
20 plurality of number of times in a gas ambient containing a foaming agent. Furthermore, there is provided a method of manufacturing a polypropylene-based resin foamed molded product, characterized by comprising molding polypropylene-based
25 resin foamed particles obtained by the above method in a mold.

[0009]

[Embodiment]

The polypropylene-based resin particles used in the present invention mainly contain a propylene copolymer of ethylene and (or) another α -olefin, and
5 the content of ethylene and (or) the other α -olefin in this copolymer is preferably 0.1 to 20 wt%, and more preferably, 0.5 to 10 wt%. If the content of ethylene and (or) the other α -olefin is less than 0.1 wt%, the copolymer becomes close to a polypropylene resin.
10 Consequently, not only the flexibility of the obtained foamed molded product lowers, but also the foaming/molding temperature rises. This is unfavorable in respect of the durability of the metal molds of a foaming machine and molding machine. On the other hand,
15 if the content of ethylene and (or) the other α -olefin exceeds 20 wt%, a crosslinking process is necessary to decrease the density of the foamed molded product. This is unpreferable in respect of the recycling properties.

20 [0010]

In the present invention, examples of α -olefin other than ethylene are those having 4 to 12 carbon atoms, such as butene-1, isobutene, pentene-1, 3-methyl-butene-1, octene-1, decene-1, and dodecene-1.

25 [0011]

Also, the polypropylene-based resin particles before the heat treatment used in the present invention

preferably have a Vicat softening temperature of 70°C to 145°C. If the Vicat softening temperature is less than 70°C, the flowability during foaming often increases, so shrinkage readily occurs immediately after foaming. This makes it difficult to obtain low-density foamed particles. In addition, if foamed resin particles like this are molded in a mold, shrinkage readily occurs after molding to make a foamed molded product having high dimensional stability difficult to obtain. On the other hand, if the Vicat softening temperature exceeds 145°C, the flowability during foaming decreases, and this increases the density of the foamed particles and makes them nonuniform. Also, when foamed particles obtained from such polypropylene-based resin particles are molded in a mold, both foamed particles and unfoamed particles mix in one molded product. This makes a foamed molded product having desired buffering properties difficult to obtain.

[0012]

The Vicat softening temperature of the polypropylene-based resin particles before the heat treatment is lower by preferably 5°C or more, and more preferably 10°C or more than the principal endothermic peak temperature on a DSC curve of the polypropylene-based resin particles. If the difference between the Vicat softening temperature before the heat

treatment and the principal endothermic peak temperature is less than 5°C, no remarkable effects can be obtained even when the polypropylene-based resin particles are heat-treated by the method of the present invention. If the foamable polypropylene-based resin particles are opened to the atmosphere and foamed after an elapse of a certain time, the density of the foamed particles often increases.

[0013]

10 The polypropylene-based resin particles used in the present invention mainly contain a propylene copolymer of ethylene and (or) another α -olefin. However, a monomer which can copolymerize with propylene or ethylene and (or) another α -olefin may also be contained in a molecule. Examples of the monomer are one or a plurality of types of monomers selected from cyclic olefins and diene-based monomers. Examples of the cyclic olefins are cyclopentene and cyclohexene, and examples of the diene-based monomers are butadiene, norbornene, 5-methylene-2-norbornene, 1,4-hexadiene, and methyl-1,4-hexadiene. Note that in the manufacture of the polypropylene-based resin particles, it is also possible to use a small amount of a vinyl monomer such as styrene, vinyl chloride, vinylidene chloride, acrylonitrile, vinyl acetate, acrylic acid, methacrylic acid, or maleic acid.

[0014].

In the present invention, the copolymer of ethylene and (or) α -olefin and propylene can be any of a binary copolymer, ternary copolymer, and multi-component copolymer. Although the copolymer can
5 be either a random copolymer or block copolymer, a random copolymer is preferable, and a random copolymer of propylene and ethylene or butene-1 is particularly favorable. In the present invention, it is also possible to use resin particles obtained by
10 melt-kneading one or a plurality of types of thermoplastic resins in the polypropylene-based resin particles.

[0015]

Examples of the thermoplastic resins which can be
15 melt-kneaded are a polypropylene homopolymer; a binary copolymer, ternary copolymer, or multi-component copolymer, which is either a random copolymer or block copolymer, of ethylene, α -olefin, cyclic olefin, and one or a plurality of types of monomers selected from
20 diene-based monomers and vinyl-based monomers, e.g., an ethylene-propylene random copolymer, ethylene-propylene block copolymer, and ethylene-propylene-butene random ternary copolymer; α -polyolefin having 4 to 12 carbon atoms such as low-density polyethylene, high-density
25 polyethylene, straight-chain, low-density polyethylene, polybutene-1, polyisobutene, polypentene-1, and polymethylpentene-1; cyclic polyolefin including, e.g.,

cyclopentene; diene-based homopolymers such as
1,2-polybutadiene and 1,3-polybutadiene; diene-based
copolymers copolymerized with, e.g., norbornene,
5-methylene-2-norbornene, 1,4-hexadiene, and
5 methyl-1,4-hexadiene; a block copolymer of butadiene
and styrene and its hydrogenated product; and
vinyl-based homopolymers and copolymers such as vinyl
chloride, vinylidene chloride, styrene, acrylonitrile,
vinyl acetate, acrylic acid, methacrylic acid, and
10 maleic acid.

[0016]

Any of the above polymers can be evenly
melt-kneaded in the polypropylene-based resin particles
at 180°C to 250°C by using a kneader such as a
15 cokneader, Banbury mixer, Brabender, uniaxial extruder,
or biaxial extruder. Of these kneaders, uniaxial and
biaxial extruders are favorable in respect of
productivity. Melt kneading can be performed a
plurality of number of times in order to well evenly
20 mix the individual compounds. Various additives, e.g.,
an antioxidant, fire retardant, fire retardant
assistant, antistatic agent, and foam adjusting agent
can be added, if desired, to the polypropylene-based
resin particles obtained as described above during
25 extrusion melt kneading, the heat treatment, or
impregnation with the foaming agent.

[0017]

The foaming modified polypropylene-based resin particles of the present invention are obtained by heat-treating the polypropylene-based resin particles within a temperature range from the principal
5 endothermic peak temperature on a DSC curve of the polypropylene-based resin particles to a temperature higher by 15°C than that. The principal endothermic peak temperature on a DSC curve of the foaming modified polypropylene-based resin particles thus obtained is
10 higher by 5°C or more, and preferably 10°C or more than that of the polypropylene-based resin particles before the heat treatment (Fig. 1). Also, the foaming modified polypropylene-based resin particles obtained by performing a heat treatment within a temperature
15 range higher by 5°C to 10°C than the principal endothermic peak temperature on a DSC curve of the polypropylene-based resin particles before the heat treatment has a DSC curve principal endothermic peak temperature which is higher by 5°C or more, and
20 preferably 10°C or more than that of the polypropylene-based resin particles before the heat treatment, and also has another endothermic peak at a temperature lower by 7°C or more than the principal endothermic peak temperature before the heat treatment
25 (Fig. 2). When the foaming modified polypropylene-based resin particles having another endothermic peak in addition to the principal

endothermic peak are used, low-density foamed particles can be obtained even if the foamable polypropylene-based resin particles are opened to the atmosphere and foamed after an elapse of a certain time.

5 [0018]

In the method of manufacturing the foaming modified polypropylene-based resin particles of the present invention, the heat treatment is performed by, e.g., dispersing the polypropylene-based resin particles in an aqueous suspension containing inorganic salt sparingly soluble in water, stirring the dispersion by a stirrer, and heating the system. The amount of polypropylene-based resin particles is preferably 100 to 20 parts by weight, and more preferably, 70 to 50 parts by weight with respect to 100 parts by weight of the aqueous suspension. Examples of the inorganic salt sparingly soluble in water are calcium phosphate and magnesium pyrophosphate. Normally, the content of the inorganic salt sparingly soluble in water is preferably 0.5 to 5 wt% with respect to the polypropylene-based resin particles. When this inorganic salt is calcium phosphate, for example, the content is normally preferably 0.5 to 2 wt% with respect to the polypropylene-based resin particles.

25 [0019]

Also, when any of these inorganic salts sparingly

soluble in water is to be used, an anionic surfactant such as soda dodecylbenzenesulfonate may also be used together. The heat-treatment temperature of the polypropylene-based resin particles falls within a temperature range from the principal endothermic peak temperature on a DSC curve of the polypropylene-based resin particles before the heat treatment to a temperature higher by preferably 15°C, and more preferably, 5°C to 10°C than that. A temperature higher than the principal endothermic peak temperature by more than 15°C is unfavorable in the manufacture because the resin particles readily combine with each other when impregnated with the foaming agent. This temperature is unpreferable also because the bulk density often increases if the foamable polypropylene-based resin particles are opened to the atmosphere and foamed after an elapse of a certain time. On the other hand, a heat-treatment temperature lower than the principal endothermic peak temperature is unfavorable because it is difficult to obtain low-density foamed particles, and the bulk density often increases if the foamable polypropylene-based resin particles are opened to the atmosphere and foamed after an elapse of a certain time.

[0020]

Although the heat-treatment time is not particularly limited, it changes in accordance with, e.g., the size (volume) and shape of the

polypropylene-based resin particles as a material. For example, if the volume of the particle is about 3.0 mm³, the heat-treatment time is preferably 0.5 hrs or more after a predetermined temperature is reached. If this
5 time is less than 0.5 hrs, the central portion and surface portion of the polypropylene-based resin particle may be unevenly heat-treated. In this case, the foam diameter may vary in each of the obtained foamed particles, and a foamed molded product obtained
10 from these foamed particles may not have any desired buffering properties.

[0021]

The foamable polypropylene-based resin particles of the present invention are normally obtained by
15 impregnating the foaming modified polypropylene-based resin particles obtained as described above with a foaming agent at a temperature lower than the Vicat softening temperature of the polypropylene-based resin particles before the heat treatment. In this manner,
20 low-density foamed particles can be obtained, and it is also possible to obtain low-density foamed particles even when the foamable polypropylene-based resin particles are opened to the atmosphere and foamed after an elapse of a certain time. This is so presumably
25 because the crystal structure of the resin particles changes when the polypropylene-based resin particles are heat-treated within the temperature range from the

principal endothermic peak temperature on a DSC curve to a temperature higher by 15°C than that. If the impregnating temperature exceeds the Vicat softening temperature of the polypropylene-based resin particles before the heat treatment, a force which stabilizes the crystal structure acts and makes it difficult to obtain low-density foamed particles as the characteristic feature of the present invention. In addition, the density undesirably increases when the foamable polypropylene-based resin particles are opened to the atmosphere and foamed after an elapse of a certain time.

[0022]

Examples of the foaming agent are volatile organic foaming agents having an atmospheric boiling point of -50°C (inclusive) to the impregnating temperature (exclusive), e.g., hydrocarbons such as propane, n-butane, i-butane, n-pentane, i-pentane, cyclopentane, pentene, and hexane, and halogenated hydrocarbons such as methylene chloride, dichlorodifluoromethane, trichloromonofluoromethane, monochlorodifluoromethane, 1,2-dichlorotetrafluoroethane, and trichlorotrifluoroethane, and inorganic gas-based foaming agents such as carbon dioxide and air. These foaming agents can be used singly or as a mixture of two or more types of them, and isobutane is particularly favorable. The addition amount of the

foaming agent changes in accordance with the type of the foaming agent. Normally, however, the addition amount is preferably 10 to 50 wt% with respect to the foaming modified polypropylene-based resin particles.

5 When the foaming agent is isobutane, for example, the addition amount is preferably about 20 to 30 wt% with respect to the foaming modified polypropylene-based resin particles.

[0023]

10 A method of impregnating the foaming modified polypropylene-based resin particles of the present invention with any of these foaming agents is not particularly limited, and both an aqueous suspension system and vapor phase system can be used. When the

15 method of impregnation in an aqueous suspension is to be used, a suspension containing inorganic salt sparingly soluble in water is used, and it is possible to add various additives normally used in the formation of foamable resin particles, in addition to the foaming

20 agent. Examples are surfactants such as soda dodecylbenzenesulfonate, foaming assistants (solvents and plasticizers), and lubricants. Examples of the inorganic salt sparingly soluble in water are the same as those usable in the heat treatment described above.

25 Examples of the foaming assistants are toluene, ethylbenzene, cyclohexane, and isoparaffin. These foaming assistants are normally added in an amount of

0.1 to 5 wt% to the foaming modified
polypropylene-based resin particles.

[0024]

Although the impregnating time of the foaming
5 agent is not particularly limited, it varies in
accordance with, e.g., the size (volume) and shape of
the foaming modified polypropylene-based resin
particles. When the volume of the particle is about
3.0 mm³, for example, impregnation is performed for 3
10 hrs or more, and preferably 4 hrs or more after a
predetermined temperature is reached. If the
impregnating time is less than 3 hrs after the
predetermined temperature is reached, an unimpregnated
portion called a core readily forms in the central
15 portion of the foaming modified polypropylene-based
resin particle. When foamed particles are formed,
therefore, both a foamed portion and unfoamed portion
may mix in one foamed particle, and a foamed molded
product obtained from such foamed particles may not
20 have any desired buffering properties.

[0025]

Note that the impregnation of the foaming agent
can be performed by cooling the heat-treated,
polypropylene-based resin particles once and then
25 heating the resin particles to a temperature lower than
the Vicat softening temperature of the resin particles,
but it may also be successively performed when the

heat-treatment temperature lowers to a temperature below the Vicat softening temperature of the polypropylene-based resin particles.

[0026]

5 The polypropylene-based resin foamed particles of the present invention are obtained by prefoaming the foamable polypropylene-based resin particles described above. The method can be performed by injecting steam having a steam pressure of about 0.5 to 5.0 kgf/cm² G
10 into a prefoaming apparatus. The injection time is generally 20 to 90 sec. Prefoaming is preferably performed after the foamable polypropylene-based resin particles are left to stand at room temperature for about one day. Also, to further decrease the bulk
15 density of the obtained polypropylene-based resin particles, it is favorable to pressurize the polypropylene-based resin foamed particles obtained as described above by holding them in a gas ambient (pressure = 1.0 to 50 kgf/cm² G) containing the foaming
20 agent for 1 to 50 hrs, and preferably 4 to 50 hrs, and then performing a prefoaming step once or a plurality of number of times. Examples of the foaming agent used in this case are the same as described above, i.e., volatile organic foaming agents having an atmospheric
25 boiling point of -50°C (inclusive) to the impregnating temperature (exclusive), e.g., hydrocarbons such as propane, n-butane, and i-butane, and halogenated

hydrocarbons such as dichlorodifluoromethane,
monochlorodifluoromethane, and
1,2-dichlorotetrafluoroethane, and inorganic gas-based
foaming agents such as carbon dioxide and air. These
5 foaming agents can be used singly or as a mixture of
two or more types of them. The method of prefoaming is
also the same as described above. The
polypropylene-based resin foamed molded product of the
present invention is obtained by molding the
10 polypropylene-based resin foamed particles obtained as
described above in a mold. This molding in a mold can
be performed in a metal mold having a desired shape and
capable of closing but incapable of hermetically
sealing foamed particles, by injecting steam having a
15 steam pressure of about 0.5 to 5.0 kgf/cm² into the
mold. A polypropylene-based resin foamed molded
product is obtained by cooling the mold with water or
air after foam molding, and removing the molded product
from the mold. Note that molding in a mold is
20 favorably performed after the polypropylene-based resin
foamed particles are left to stand at room temperature
for about one day, and held in a gas ambient (pressure
= 1.0 to 50 kgf/cm² G) containing the foaming agent for
1 to 24 hrs, and preferably 4 to 24 hrs.

25 [Examples]

The present invention will be explained in more
detail below by way of its examples, but is not at all

limited to these examples.

[0027]

Example 1

(Method of manufacturing foaming modified

5 polypropylene-based resin particles)

[0028]

50 L of water, 600 g of calcium phosphate as a dispersant, and 30 g of soda dodecylbenzenesulfonate as an active agent were placed in an autoclave having a
10 volume of 100 L. In addition, 15 g of amide ethylenebisstearate were added as a foam adjusting agent, thereby preparing an aqueous medium. Also, 30 kg of pellets (polypropylene-based resin particles) 2.0 mm in length and 1.5 mm in diameter obtained by a
15 uniaxial extruder from a propylene-ethylene random copolymer resin containing 4 wt% of an ethylene component, and having a DSC curve principal endothermic peak temperature of 135°C which was obtained by scanning differential calorimetry, and a Vicat
20 softening temperature of 117°C, were suspended in the aqueous medium, and the suspension was stirred at a stirring speed of 150 rpm. After that, the mixture was heated to 145°C, held at that temperature for 1 hr, and then cooled to 40°C. The obtained mixture was
25 dehydrated to extract a product, thereby obtaining foaming modified polypropylene-based resin particles.

[0029]

The principal endothermic peak temperature of a DSC curve of the foaming modified polypropylene-based resin particles was 156°C, i.e., higher by 21°C than that of the polypropylene-based resin particles before
5 the heat treatment. Also, the foaming modified polypropylene-based resin particles had another endothermic peak in addition to the principal endothermic peak, and the endothermic peak temperature of this peak was 123°C.

10 (Method of manufacturing foamable polypropylene-based resin particles)

Then, 3 L of water, 30 g of calcium phosphate as a dispersant, and 1 g of soda dodecylbenzenesulfonate as a surfactant were placed in an autoclave having a
15 volume of 5 L to prepare an aqueous medium. 1 kg of the foaming modified polypropylene-based resin particles obtained as described above was suspended in the aqueous medium, and the suspension was stirred at a stirring speed of 350 rpm. After that, 250 g of
20 isobutane were injected by using a nitrogen pressure. The mixture was heated to 80°C, held at that temperature for 4 hr, and cooled to 25°C. The obtained mixture was then dehydrated to extract a product, thereby obtaining foamable polypropylene-based resin
25 particles.

[0030]

The obtained foamable polypropylene-based resin

particles were removed from the autoclave and dehydrated. When 10, 30, and 60 min elapsed, the foamable polypropylene-based resin particles were prefoamed by heating by a prefoaming machine in an ambient at a steam pressure of 0.5 to 5.0 kgf/cm² G for 30 sec, thereby obtaining different types of foamed particles. The bulk density of the foamed particles of each type was measured. Table 1 shows the smallest value of the measured bulk densities. These foamed particles had a low density and high uniformity. In addition, even when the foamable polypropylene-based resin particles were opened to the atmosphere and foamed after an elapse of a certain time, the density of the obtained foamed particles remained almost unchanged. In this example, DSC curves were obtained by the following method.

[0031]

That is, 3 to 7 mg of polypropylene-based resin particles before a heat treatment were heated from 30°C to 220°C at a heating rate of 10°C/min by using a scanning differential calorimeter (SEIKO DSC 200), and the principal endothermic peak temperature of the resin particles was calculated from the obtained DSC curve.

[0032]

As shown in Fig. 1, the principal endothermic peak temperature of foaming modified polypropylene-based resin particles heat-treated within

the temperature range from the principal endothermic peak temperature of the DSC curve, which was obtained by scanning differential calorimetry, of the polypropylene-based resin particles before the heat
5 treatment to a temperature higher by 15°C than that rose by 5°C or more from that before the heat treatment.
[0033]

Foamed modified polypropylene-based resin particles obtained by heat-treating polypropylene-based
10 resin particles within the temperature range from a temperature higher by 5°C than the principal endothermic peak temperature on a DSC curve of the polypropylene-based resin particles to a temperature higher by 10°C than that had a DSC curve principal
15 endothermic peak temperature which shifted by 5°C or more from that before the heat treatment, and also had another endothermic peak at a temperature lower by 7°C or more (Fig. 2). When the foaming modified polypropylene-based resin particles like this are used,
20 the change in bulk density is extremely small even if the obtained foamable polypropylene-based resin particles are opened to the atmosphere and foamed after an elapse of a certain time.
[0034]

25 Also, polypropylene-based resin particles whose DSC curve principal endothermic peak temperature was measured were cooled from 220°C to 30°C at a cooling

rate of 10°C/min once, and then heated from 30°C to 220°C at a heating rate of 10°C/min again by using the scanning differential calorimeter (SEIKO DSC 200). The principal endothermic peak temperature of the obtained DSC curvet was substantially equal to that of the resin particles before the heat treatment. Therefore, the principal endothermic peak temperature of the foaming modified polypropylene-based resin particles rose from that of the polypropylene-based resin particles because the heat treatment was performed within the temperature range described above.

[0035]

The Vicat softening temperature was obtained by a method complying with JIS K-7206. That is, a 10 × 10 × 5-mm sample was cut out from a 30 × 40 × 5-mm plate-like specimen formed by an injection molding machine. A heat distortion tester (manufactured by Toyo Seiki Seisaku-Sho) was used to heat a heat transfer medium at 10°C/min while a load of 250 g was kept applied via a needle-like indenting tool vertically placed on the sample in a heating bath. The temperature of the heat transfer medium when the needle-like indenting tool penetrated 1 mm was defined as the Vicat softening temperature.

[0036]

The bulk density of the foamed particles was calculated by the following equation by a method

complying with JIS K 6767.

Bulk density (g/cm^3) = W/V

V: the bulk volume (cm^3) of the foamed particles

W: the mass (g) of the foamed particles

5 [0037]

Examples 2 & 3

Foamable polypropylene-based resin particles were obtained following the same procedures as in Example 1 except that the heat-treatment temperatures were as
10 shown in Table 1. The principal endothermic peak temperature of a DSC curve of the heat-treated foaming modified polypropylene-based resin particles was 147°C in Example 2, and 140°C in Example 3. These foaming modified polypropylene-based resin particles had no
15 distinct peak corresponding to the endothermic peak other than the principal endothermic peak in Example 1.

[0038]

The obtained foamable polypropylene-based resin particles were removed and prefoamed when 10, 30, and
20 60 min elapsed, thereby obtaining different types of foamed particles. The bulk density of the foamed particles of each type was measured. Table 1 shows the smallest value of the measured bulk densities.

Examples 4 & 5

25 Foamable polypropylene-based resin particles were obtained following the same procedures as in Example 1 except that the temperatures for impregnation of the

foaming agent were as shown in Table 1.

[0039]

The obtained foamable polypropylene-based resin particles were removed and prefoamed when 10, 30, and 5 60 min elapsed, thereby obtaining different types of foamed particles. The bulk density of the foamed particles of each type was measured. Table 1 shows the smallest value of the measured bulk densities.

Examples 6 & 7

10 Foamable polypropylene-based resin particles were obtained following the same procedures as in Example 1 except that the ethylene contents, heat-treatment temperatures, impregnating temperatures, and impregnating pressures were as shown in Table 1.

15 [0040]

The obtained foamable polypropylene-based resin particles were removed and prefoamed when 10, 30, and 60 min elapsed, thereby obtaining different types of foamed particles. The bulk density of the foamed 20 particles of each type was measured. Table 1 shows the smallest value of the measured bulk densities.

Example 8

Foamable polypropylene-based resin particles were obtained following the same procedures as in Example 1 25 except that a propylene-ethylene block copolymer resin was used as polypropylene-based resin particles, and the heat-treatment temperature, impregnating

temperature, and impregnating pressure were set as shown in Table 1.

[0041]

The obtained foamable polypropylene-based resin particles were removed and prefoamed when 10, 30, and 60 min elapsed, thereby obtaining different types of foamed particles. The bulk density of the foamed particles of each type was measured. Table 1 shows the smallest value of the measured bulk densities. In each example, as shown in Table 1, the foaming modified polypropylene-based resin particles were impregnated with the foaming agent at a temperature lower than the Vicat softening temperature of the polypropylene-based resin particles before the heat treatment. Therefore, the foamable polypropylene-based resin particles obtained in each example were substantially not crosslinked, and superior in recycling properties.

[0042]

Even when the foamable polypropylene-based resin particles manufactured by each example were opened to the atmosphere and foamed after an elapse of a certain time, the decrease in bulk density was extremely small. In addition, the foamed particles manufactured from these resin particles had a low density and high uniformity. That is, the foamable polypropylene-based resin particles of the present invention have the characteristic that the bulk density of the foamed

particles changes extremely little with time after pressure opening.

[0043]

Comparative Examples 1 & 2

5 Foamable polypropylene-based resin particles were obtained following the same procedures as in Example 1 except that the heat-treatment temperatures were as shown in Table 1. The obtained foamable polypropylene-based resin particles were removed and
10 prefoamed when 10, 30, and 60 min elapsed, thereby obtaining different types of foamed particles. The bulk density of the foamed particles of each type was measured. Table 1 shows the smallest value of the measured bulk densities.

15 [0044]

Comparative Example 3

 It was attempted to manufacture foamable polypropylene-based resin particles following the same procedures as in Example 1 except that
20 polypropylene-based resin particles having an ethylene content as shown in Table 1 were used, and the heat-treatment temperature was set as shown in Table 1. Table 1 shows the results.

[0045]

25 Comparative Example 4

 Foamable polypropylene-based resin particles were obtained following the same procedures as in Example 1

except that no heat treatment was performed, and it was tried to foam the foamable polypropylene-based resin particles. Table 1 shows the results.

[0046]

[Table 1]

	Ethylene Component content (wt%)	Type of Copolymer	Endothermic Peak Temperature before Heat Treatment (°C)	Vicat Softening Temperature (°C)	Heat- treatment Temperature (°C)
Example 1	4	Random	135	117	145
Example 2	4	Random	135	117	135
Example 3	4	Random	135	117	150
Example 4	4	Random	135	117	145
Example 5	4	Random	135	117	145
Example 6	0.5	Random	150	145	155
Example 7	20	Random	135	70	140
Example 8	0.5	Block	155	145	160
Comparative Example 1	4	Random	135	117	130
Comparative Example 2	4	Random	135	117	155
Comparative Example 3	30	Random	135	55	140
Comparative Example 4	4	Random	135	117	-

	Peak Temperature after Heat Treatment (°C)		Impregnating Temperature (°C)	Impregnating Pressure (kgf/cm ² G)
	Highest Endothermic Peak	Newly Generated Peak		
Example 1	156	123	80	13
Example 2	147	-	80	13
Example 3	140	-	80	13
Example 4	156	123	40	6
Example 5	156	123	115	21
Example 6	160	140	100	18
Example 7	150	128	40	6
Example 8	165	143	100	18
Comparative Example 1	135	-	80	13
Comparative Example 2	-	-	-	-
Comparative Example 3	-	-	-	-
Comparative Example 4	135	-	80	13

	Bulk Density of Foamed Particles with Time (g/cm ³)					Total Evaluation
	Immediately after Pressure Opening	In 10 min	In 30 min	In 60 min	Maximum Value - Minimum Value	
Example 1	0.043	0.045	0.048	0.050	0.007	○
Example 2	0.059	0.067	0.077	0.091	0.032	△
Example 3	0.056	0.063	0.071	0.083	0.027	△
Example 4	0.043	0.045	0.048	0.050	0.007	○
Example 5	0.043	0.048	0.050	0.053	0.010	○
Example 6	0.056	0.063	0.067	0.071	0.015	△
Example 7	0.059	0.063	0.067	0.077	0.018	△
Example 8	0.063	0.071	0.077	0.083	0.020	△
Comparative Example 1	0.083	0.125	0.250	0.500	0.417	×
Comparative Example 2	Particles melted and combined with each other when heat-treated					×
Comparative Example 3	Particles melted and combined with each other when heat-treated					×
Comparative Example 4	Did not foam					×

(Notes)

○ The change in bulk density of the foamed particles
with time was small

△ The change in bulk density of the foamed particles

with time was small, but the bulk density of the foamed particles immediately after opening was high

× The change in bulk density of the foamed particles with time was large

5 ×× The particles did not foam, or unfoamed particles mixed

[0047]

As shown in Table 1, when the foaming modified polypropylene-based resin particles obtained by
10 heat-treating the polypropylene-based resin particles within the temperature range from the principal endothermic peak temperature of the polypropylene-based resin particles before the heat treatment to a temperature higher by 15°C than that were impregnated
15 with the foaming agent at a temperature lower than the Vicat softening temperature of the polypropylene-based resin particles before the heat treatment, the bulk density changed extremely little with time even if the obtained foamable polypropylene-based resin particles
20 were opened to the atmosphere and foamed after an elapse of a certain time. Furthermore, the foamed particles manufactured from these foamable polypropylene-based resin particles had a low density and high uniformity.

25 [0048]

Example 9

Foamable polypropylene-based resin particles

obtained following the same procedures as in Example 1 were dehydrated and placed in a prefoaming machine, and steam was injected at a steam pressure of 4.3 kgf/cm² G for about 30 sec, thereby obtaining polypropylene-based resin foamed particles. In addition, the obtained foamed particles were held in a gas ambient (5.0 kgf/cm² G) containing the foaming agent for one day and placed in a mold, and steam was injected at a steam pressure of 4.4 kgf/cm² G for about 30 sec, thereby obtaining a polypropylene-based resin foamed molded product. The heat resistances to steam of the obtained polypropylene-based resin foamed particles and polypropylene-based resin foamed molded product were measured. As the heat resistance to steam of the polypropylene-based resin foamed particles, a steam pressure required when the foamable polypropylene-based resin particles were prefoamed was measured. As the heat resistance to steam of the polypropylene-based resin foamed molded product, a steam pressure required when the polypropylene-based resin foamed particles were molded in a mold was measured.

[0049]

Examples 10 - 12

Polypropylene-based resin foamed particles and polypropylene-based resin foamed molded products were obtained following the same procedures as in Example 9 except that the heat-treatment temperatures were as

shown in Table 2. Also, the heat resistances to steam of foamable polypropylene-based resin particles and the polypropylene-based resin foamed particles were measured. Table 2 shows the results.

5 [0050]

Examples 13 & 14

Polypropylene-based resin foamed particles and polypropylene-based resin foamed molded products were obtained following the same procedures as in Example 9
10 except that the temperatures for impregnation of the foaming agent were as shown in Table 2. Also, the heat resistances to steam of foamable polypropylene-based resin particles and the polypropylene-based resin foamed particles were measured. Table 2 shows the
15 results.

[0051]

Examples 15 & 16

Polypropylene-based resin foamed particles and polypropylene-based resin foamed molded products were
20 obtained following the same procedures as in Example 9 except that the ethylene contents were as shown in Table 2. Also, the heat resistances to steam of foamable polypropylene-based resin particles and the polypropylene-based resin foamed particles were
25 measured. Table 2 shows the results.

[0052]

Example 17

The polypropylene-based resin foamed particles obtained in Example 9 were held in a gas ambient (5.0 kgf/cm² G) containing the foaming agent for one day, opened to the atmosphere, and prefoamed by injecting steam at a steam pressure of 4.4 kgf/cm² G for about 30 sec, thereby obtaining polypropylene-based resin foamed particles. In addition, the obtained foamed particles were held in a gas ambient (5.0 kgf/cm² G) containing the foaming agent for one day, opened to the atmosphere, and molded in a mold by injecting steam at a steam pressure of 4.4 kgf/cm² G into the mold for about 30 sec, thereby obtaining a polypropylene-based resin foamed molded product. Also, the steam pressures (first time and second time) required to prefoam foamable polypropylene-based resin particles and the steam pressure required for the molding in the mold were measured. Table 2 shows the results. The polypropylene-based resin foamed particles and polypropylene-based resin foamed molded product obtained in the example were substantially not crosslinked and superior in recycling properties, and had a low bulk density as shown in Table 2. Also, as shown in Fig. 3, the heat resistance to steam (the steam pressure when foamable polypropylene-based resin particles obtained from polypropylene-based resin particles having a principal endothermic peak temperature of 135°C were prefoamed) of the

polypropylene-based resin foamed particles changed in accordance with the change in heat-treatment temperature of the polypropylene-based resin particles, and hence could be controlled by adjusting the
5 heat-treatment temperature.

[0053]

Comparative Examples 5 & 6

Polypropylene-based resin foamed particles and polypropylene-based resin foamed molded products were
10 obtained following the same procedures as in Example 9 except that the heat-treatment temperatures of polypropylene-based resin particles were as shown in Table 2. Also, the heat resistances to steam of
15 foamable polypropylene-based resin particles and the polypropylene-based resin foamed particles were measured. Table 2 shows the results.

[0054]

Comparative Example 7

Polypropylene-based resin foamed particles and a
20 polypropylene-based resin foamed molded product were obtained following the same procedures as in Example 9 except that the temperature for impregnation of the foaming agent was as shown in Table 2. Also, the heat resistances to steam of foamable polypropylene-based
25 resin particles and the polypropylene-based resin foamed particles were measured. Table 2 shows the results.

[0055]

Comparative Example 8

Polypropylene-based resin foamed particles and a polypropylene-based resin foamed molded product were
5 obtained following the same procedures as in Example 9 except that polypropylene-based resin particles were not heat-treated. Also, the heat resistances to steam of foamable polypropylene-based resin particles and the polypropylene-based resin foamed particles were
10 measured. Table 2 shows the results.

[0056]

[Table 2]

	Ethylene Component Content (wt%)	Endothermic Peak Temperature before Heat Treatment (°C)	Vicat Softening Temperature (°C)	Heat- treatment Temperature (°C)	Principal Endothermic Peak Temperature after Heat Treatment (°C)
Example 9	4	135	117	145	156
Example 10	4	135	117	135	147
Example 11	4	135	117	140	153
Example 12	4	135	117	150	140
Example 13	4	135	117	145	156
Example 14	4	135	117	145	156
Example 15	0.5	150	145	155	160
Example 16	20	135	70	140	150

Example 17	4	135	117	145	156
Compara tive Example 5	4	135	117	130	135
Compara tive Example 6	4	135	117	155	-
Compara tive Example 7	4	135	117	145	156
Compara tive Example 8	4	135	117	-	135

	Impregnating Temperature (°C)	Prefoaming			
		1st Time		2nd Time	
		Steam Pressure during Foaming (kgf/cm ² G)	Bulk Density of Foamed Particles (g/cm ³)	Steam Pressure during Foaming (kgf/cm ² G)	Bulk Density of Foamed Particles (g/cm ³)
Example 9	80	4.3	0.059	-	-
Example 10	80	3.3	0.067	-	-
Example 11	80	4.0	0.059	-	-
Example 12	80	3.0	0.059	-	-
Example 13	40	4.3	0.058	-	-
Example 14	115	4.0	0.058	-	-
Example 15	100	5.0	0.058	-	-
Example 16	40	3.5	0.059	-	-
Example 17	80	4.3	0.059	4.4	0.025
Comparative Example 5	80	2.6	0.111	-	-
Comparative Example 6	-	Particles melted and combined with each other when heat-treated			
Comparative Example 7	120	3.0	0.083	-	-
Comparative Example 8	80	2.5	Unfoamed particles mixed		

	Steam Pressure during Molding (kgf/cm ² G)	Total Evaluation
Example 9	4.4	○
Example 10	3.4	○
Example 11	4.1	○
Example 12	3.1	○
Example 13	4.4	○
Example 14	4.1	○
Example 15	5.2	○
Example 16	3.5	○
Example 17	4.3	○
Compara tive Example 5	2.6	×
Compara tive	Particles melted and combined with each other when	××

Example 6	heat-treated	
Compara tive Example 7	3.1	×
Compara tive Example 8	Unfoamed particles mixed	×

Notes

○ Low-density foamed particles were obtained,
indicating the effect of modification

× Low-density foamed particles were difficult to
5 obtain

×× Unfoamed particles mixed, or manufacturing
problems arose

[0057]

As shown in Table 2, the heat resistances to
10 steam of the polypropylene-based resin formed particles
and polypropylene-based resin foamed molded product can
be controlled by adjusting the heat-treatment
temperature of polypropylene-based resin particles.

[0058]

15 [Effects of the Invention]

The foamable polypropylene-based resin particles

of the present invention are substantially not crosslinked and superior in recycling properties, and foamed particles which change the bulk density extremely little are obtained even when the foamable
5 polypropylene-based resin particles are opened to the atmosphere and foamed after an elapse of a certain time. In addition, polypropylene-based resin foamed particles and a polypropylene-based resin foamed molded product manufactured from the resin particles are substantially
10 not crosslinked and superior in recycling properties, and have a low density and high uniformity. Also, the heat resistances to steam of these foamed particles and foamed molded product can be controlled by adjusting the heat-treatment temperature of the
15 polypropylene-based resin particles.

[Brief Description of the Drawings]

[Fig. 1]

Fig. 1 is a graph showing the principal endothermic peak temperatures on DSC curves of polypropylene-based
20 resin particles and foaming modified polypropylene-based resin particles.

[Fig. 2]

Fig. 2 is a graph showing foamed modified polypropylene-based resin particles having another
25 endothermic peak in addition to the principal endothermic peak on a DSC curve.

[Fig. 3]

Fig. 3 is a graph showing the relationship between the heat-treatment temperature of polypropylene-based resin particles having a principal endothermic peak of 135°C and the steam pressure during prefoaming of foamable
5 polypropylene-based resin particles obtained from the resin.

FIG. 1

- (1): PRINCIPAL ENDOTHERMIC PEAK TEMPERATURE**
- (2): PRINCIPAL ENDOTHERMIC PEAK UNIQUE TO RESIN BEFORE
HEAT TREATMENT**
- 5 (3): PRINCIPAL ENDOTHERMIC PEAK AFTER HEAT TREATMENT**

FIG. 2

- (1): TEMPERATURE**

10 FIG. 3

- (1): STEAM PRESSURE IN PREFOAMING**
- (2): HEAT-TREATMENT TEMPERATURE**
- (3): PRINCIPAL ENDOTHERMIC PEAK UNIQUE TO RESIN BEFORE
HEAT TREATMENT WAS 135°C**

